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TiO_2: Cr nanopowders for hydrogen sensing

B. Lyson[a*], P. Gwizdz[a], A. Czapla[a], M. Lubecka[a], K. Zakrzewska[a], K. Biernacka[b], M. Radecka[c], K. Michalow-Mauke[d], T. Graule[d], A. G. Balogh[e], S. Lauterbach[f], H.-J. Kleebe[f]

[a]*Faculty of Electrical Engineering, Automatics, Computer Science and Electronics, AGH University of Science and Technology*
[b]*Faculty of Physics and Applied Computer Science, AGH University of Science and Technology*
[c]*Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Cracow, Poland*
[d]*EMPA, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, Dubendorf, Switzerland*
[e]*Institute of Materials Science, Technische Universität Darmstadt, Germany*
[f]*Institute for Applied Geosciences, Technische Universität Darmstadt, Germany*

Abstract

The aim of this research was to use nanocrystalline TiO_2 and TiO_2: Cr (0.1–10 at. % Cr) obtained by Flame Spray Synthesis, FSS, for hydrogen sensing. Morphological properties of nanopowders were investigated by Brunauer–Emmett–Teller, BET, adsorption isotherms, X-ray Diffraction, XRD, Scanning Electron Microscopy, SEM, and Transmission Electron Microscopy, TEM. Nanosensors were prepared in a form of circular tablets by pressing the nanopowder at the pressure of 25 MPa and heating up to 400°C. Dynamic changes in the electrical resistance $\Delta R/R_o$ upon hydrogen exposure were detected over low-to-medium concentration range of 50-3000 ppm at 200-400°C. The influence of particle size and Cr content on the sensor response was studied.

TiO_2 nanopowders, Cr dopant, gas sensors, hydrogen detection, Flame Spray Synthesis

1. Introduction

Nanoscience and nanotechnology seem to hold the key solutions to the issue of the improvement of the resistive gas sensor operating parameters. It is impossible to overestimate the role of nanomaterials in modifying sensitivity, selectivity, response time and other features extremely important as far as we consider a reliable gas sensor. Furthermore, nanosensors can work over lower temperature range as

* Corresponding author. Tel.:+48 12 617-2901; fax:+48 12 633-23-98.
E-mail address: *lyson@novell.ftj.agh.edu.pl*

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compared with their microcrystalline counterparts what is especially important as far as we consider power consumption and reducing operating costs. Among many metal oxide candidates (TiO_2, SnO_2, WO_3, and ZnO) for gas detection, TiO_2 is a unique and well-promising material. Reversible and large changes ΔR in the electrical resistance along with the inherent chemical stability at high temperatures and in harsh environments are widely exploited in the resistive-type gas sensors based on TiO_2. Basic parameters characterizing gas sensor performance such as sensitivity, selectivity and response time of TiO_2-based sensors can be optimized by choosing the appropriate type and level of doping [1]. Recently, many attempts have been undertaken to exploit the influence of a trivalent chromium dopant acting as an acceptor type impurity on the electrical and gas sensing properties of TiO_2 [2]. According to the literature, doping with metals, e.g. Cr affects the response time, sensitivity and the initial resistivity (baseline) of the sensor [2,3]. Usually, TiO_2 behaves like n-type semiconductor thus is considered a promising candidate for detection of reducing gases such as hydrogen, carbon dioxide or methane. However under certain conditions n → p transition may occur in TiO_2 [4]. This is beneficial for detection of oxidizing gases such as oxygen and NO_x where the sign of the resistance change can be reversed in p-type material [3]. The aim of this work was to study gas sensing propertied of nanocrystalline TiO_2:Cr nanopowders obtained by Flame Spray Synthesis (FSS). This method was used because it allowed us to obtain crystalline powders in a single step thanks to a high temperature in the flame [5-7]. The effect of chromium concentration and crystallite size on the sensor dynamic responses to hydrogen has been the object of the investigations. Hydrogen, as a proposed fuel of the future, has to be detected at very small quantities.

2. Experimental

Nanopowders of TiO_2:Cr with up to 10 at.% Cr were obtained by Flame Spray Synthesis (FSS) as described in detail in [5,6]. Titanium tetra-isopropoxide TTIP and solution of chromium acetyloacetonate CHAA in m-xylene were used as precursors of Ti and Cr, respectively. Specific surface area, SSA, of nanopowders was determined from nitrogen adsorption BET (Brunauer-Emmett-Teller) isotherms obtained with a Beckman-Coulter SA3100. Grain size of nanopowders was determined from the SSA data while the dimensions of crystallites were analyzed on the basis of XRD patterns recorded with the help of X'Pert MPD Philips diffractometer. Transmission Electron Microscopy TEM of nanopowders was performed. Nanosensors were prepared in a form of circular tablets calcined from nanopowders at the pressure of 25 MPa and temperature of 400°C. Planar silver electrodes were applied 5 mm apart. Dynamic changes in the electrical resistance $\Delta R/R_o$ upon hydrogen exposure were detected over low-to-medium concentration range of 50-3000 ppm at 200-400°C in a custom-made system described in detail elsewhere [8]. Air, at the flow rate of 120 sccm, was used as a reference gas. Sensor response S was defined as $S=1-R/R_0$, where R represented the electrical resistance upon interaction with gas and R_0 was the electrical resistance measured in air.

3. Results and discussion

Flame Spray Synthesis, FSS provided us with nanocrystalline powders of undoped TiO_2 and Cr-doped TiO_2 with large specific surface area SSA over the range of 37-126 m^2/g and small crystallite size of 6-27 nm. TEM images (Fig.1.) reveal particles with the size decreasing systematically from 40 nm to 10 nm with the increasing Cr content. This is a consequence of a dilution effect described in detail in [6]. As discussed previously [5,7], two polymorphic forms of TiO_2, namely rutile and anatase are present. The fraction of anatase largely dominates over rutile, but the rutile amount increases slightly with the addition of Cr.

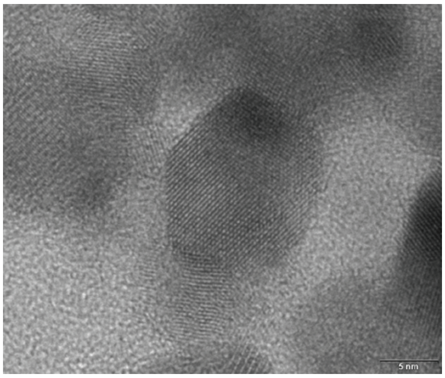

Fig. 1. High resolution TEM image of TiO_2: 5 at. % Cr nanopowder.

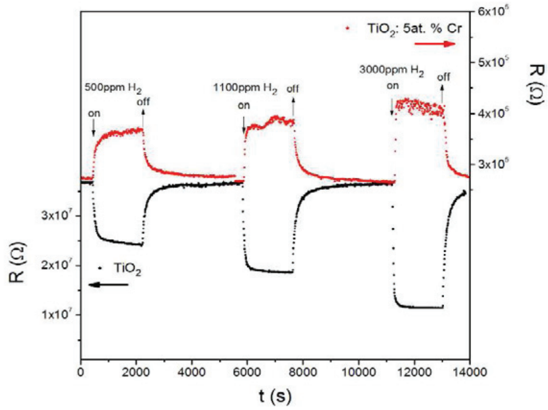

Fig. 2. Dynamic changes in the electrical resistance R for TiO_2 (left hand scale) and TiO_2:5 at. % Cr (right hand scale) nanosensors upon exposure to 500, 1100 and 3000 ppm H_2 at constant temperature of 350°C.

Up to 10 at.% Cr none of the secondary phases, neither chromium oxide nor chromium titanates have been identified. This is compatible with the reported solubility limit of Cr^{3+} in TiO_2 and the fact that the ionic radii of Cr^{3+} and Ti^{4+} are very similar [9]. Fig. 2 presents changes of the electrical resistance of undoped TiO_2 and TiO_2 doped with 5 at. % Cr sensor materials upon interaction with the reducing gas H_2 as a function of time at a constant temperature of 350°C. Large and reproducible responses of the sensors follow the step changes 0-500 ppm-0, 0-1100 ppm-0, 0-3000 ppm-0 in H_2 concentration. As we can see, there is a systematic decrease in the electrical resistance R for undoped TiO_2 upon exposure to H_2, whereas for the TiO_2:5 at. % Cr the same parameter R increases upon interaction with H_2. Such observed changes in R upon adsorption of hydrogen indicate that undoped TiO_2 behaves as an n-type semiconductor, whereas starting from 5 at. % Cr the samples exhibit p-type conductivity. Moreover, as one can see in Fig.2, incorporation of 5 at. % Cr into TiO_2 causes significant decrease, by two orders of magnitude as compared with undoped TiO_2, in the baseline electrical resistance R_0 of the material in air.

Chromium dopant modifies the electronic structure of TiO_2 and forms localized acceptor levels in the forbidden band gap. This modifies the concentration of electrons and electron holes and leads to a decrease in the electrical resistance R_0 in air over low-to-medium temperature range. Substitutional incorporation of Cr^{3+} can be described by the following reaction:

$$Cr_2O_3 \rightarrow 2Cr_{Ti} + V_O^{\bullet\bullet} + 3O_O + 2e^{'}$$

where $V_O^{\bullet\bullet}$ denotes doubly ionized oxygen vacancy, Cr_{Ti} represents Cr substitution at Ti sites.

Because of the observed sign reversal of the sensor response S within the range of 1 at.% and 5 at.% Cr, in order to compare the sensors sensitivity, the absolute value |S| is plotted in Fig 3. The results indicate that at 250°C the best sensor response is obtained for 5 at% of Cr. For undoped TiO_2 the lowest temperature at which the baseline resistance could be measured was 300⁰C. This relatively high operating temperature for the undoped TiO_2 can be lowered to 210-250°C by adding Cr. Fig. 4 demonstrates the response S of the TiO_2:Cr nanosensors as a function the operating temperature for a given change in the hydrogen concentration from 0 to 200 ppm. As can be noticed, the operating temperature below 250°C can be reached for TiO_2: 1 at. % Cr, TiO_2: 5 at. % Cr and TiO_2: 10 at. % Cr. This effect is, to a large extent, due to doping through the decreased baseline resistance in air.

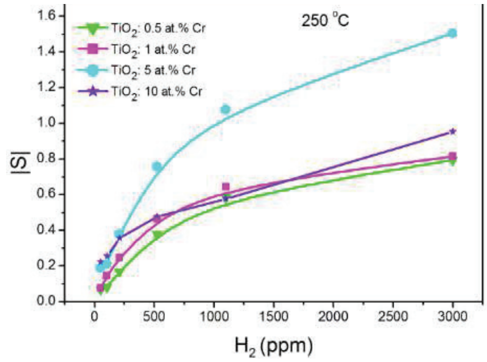

Fig. 3. Absolute value of the gas sensor response |S| as a function of hydrogen concentration at a constant temperature of 250°C.

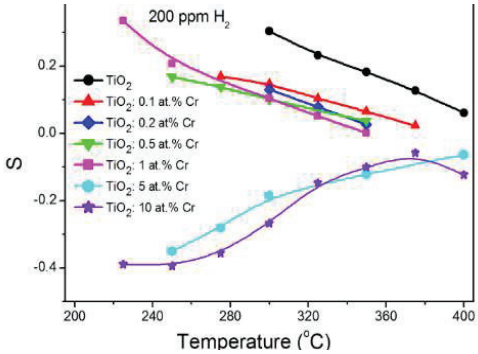

Fig. 4. Gas sensor response S as a function of operation temperature at a constant hydrogen concentration of 200 ppm.

4. Conclusions

The results obtained in the course of these studies allow to formulate the following conclusions. Crystalline nanopowders of mostly anatase TiO_2, grown by Flame Spray Synthesis, are characterized by large specific surface area and small crystallite size depending on Cr loading. Nanosensors obtained from TiO_2:Cr nanopowders show promising dynamic characteristics in response to hydrogen. The sensor responses are large and reproducible. The electrical resistance R decreases upon hydrogen exposure as long as Cr concentration does not exceed 1 at.% Cr while the reversed effect is observed at 5 and 10 at.% Cr. The sensor performance in the latter case clearly improves with a decrease in the operating temperature. Incorporation of 1 at.% and 5 at.% of Cr into TiO_2 allows to reach lower baseline resistance in air over the temperature range of 210-250°C thus proving sensor sensitivity to hydrogen

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